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Art Unit	: 1712	Customer No.: 035811
Examiner	: Kuo Liang Peng	
Serial No.	: 10/089,948	
Filed	: April 4, 2002	
Inventor	: Hideo Matsuoka	Docket No.: 1098-02
	: Mitsushige Hamaguchi	
	: Kazuhiko Kobayashi	Confirmation No.: 8953
Title	: RESIN STRUCTURE AND USE THEREOF	Dated: August 22, 2006

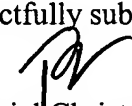
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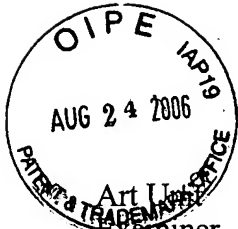
Sir:

Following up on the Response mailed August 17, 2006, we now enclose a copy of the article referred to bridging pages 6 and 7 of the Response entitled "Studies on miscibility and phase-separated morphology of nylon 4,6/poly (phenylene sulfide) blend under shear flow" by Jung-Bum An et al., J. Macromol-SCI.-Physics, B41(3), 407-418 (2002).

Respectfully submitted,


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August 22, 2006

STUDIES ON MISCIBILITY AND PHASE-SEPARATED MORPHOLOGY OF NYLON 4,6/POLY(PHENYLENE SULFIDE) BLEND UNDER SHEAR FLOW

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ABSTRACT

The effects of simple shear flow on the phase behavior of nylon 4,6/poly(phenylene sulfide) (PA4,6/PPS) blends, which are completely immiscible in the measured temperature range in the quiescent state, have been investigated by a shear apparatus. In the shear experiments, the miscibility region appeared for the PA4,6/PPS 80/20 composition at a high shear rate, above 150 sec^{-1} at 310°C and 189 sec^{-1} at 320°C . On the other hand, the shear-induced mixing did not take place for the other measured compositions (PA4,6/PPS 50/50 and 20/80). Therefore, the shear-induced mixing took place in only a small region although there existed no single-phase region in the quiescent state. The single-phase specimen under the shear flow is again phase separated during annealing without shear flow. The phase separation took place via spinodal decomposition and a regular, phase-separated morphology was observed.

Key Words: Nylon 4,6; Poly(phenylene sulfide); Shear flow; Shear-induced mixing; Spinodal decomposition

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INTRODUCTION

Recently, there has been considerable attention to the flow field effect on polymer blends (1–22). Most industrial products for polymer blends are manufactured under flow fields. It is necessary, in the industrial application of polymer blends, to determine the effect of shear flows on polymer blends. Simple shear flow brings some polymer blends into a single-phase state, which is called the shear-induced phase mixing (2–13). On the contrary, simple shear flow can also bring single-phase polymer blends into phase separation, which is called shear-induced phase demixing or separation (14,15). Sometimes both phenomena occur together in the same polymer blend according to the shear rate or the composition of the blend (16,17).

Suppose that a polymer blend is sheared in the extruder; large droplets are broken into smaller droplets due to the hydrodynamic forces of the shear flow. However, the small droplets collide and grow into larger droplets due to the thermodynamic forces of lowering the interface free energy. Thus, the balance of these two effects determines the steady-state droplet size as a function of the shear rate. These effects of shear fields on the phase behavior are theoretically interpreted in terms of the enhancement of concentration fluctuations (15) and the elastic contribution to the free energy of mixing (18–22).

Poly(phenylene sulfide) (PPS) has a high melting point ($T_m = 280^\circ\text{C}$) and is one of the most important engineering thermoplastic polymers. It has various good physical properties, such as high chemical and heat resistance, due to the high T_m . It is applied for rigid and heat resistant parts in automotive and electronic goods. However, PPS has some shortcomings, such as low toughness and residual flash in processing. On the other hand, Nylon 4,6 (PA4,6) also has a high T_m ($= 295^\circ\text{C}$) and good physical properties such as high chemical and heat resistance. It is sometimes used as a substitute for PPS, but the physical properties become worse with water absorption.

The blend of these polymers is very interesting because there is a possibility that the shortcomings of each polymer are overcome without a decrease in the high T_m . Usually, simple blends of polymers make the physical properties worse because of immiscibility. Therefore, compatibilizers for mixtures are necessary. The blend of PPS/PA4,6 is also immiscible. Fortunately, however, this blend shows good physical properties without any compatibilizer, and is already used commercially. For example, the blister resistance was improved by mixing PPS with PA4,6. The good compatibility may be due to the small difference of solubility parameter between the two polymers or the flow field may play an important role in the phase morphology. Thus, we examine the miscibility under the shear field. In this study, the miscibility and phase morphology of PA4,6/PPS blend under simple shear flow were measured because the investigation of the effect of shear flow during extruding in actual processing is very difficult.

EXPERIMENTAL

The PA4,6 in this study was a commercial polymer from JSR Co., with $M_w = 48,000$. The linear type PPS was also a commercial polymer, from Tohpren Co. with $M_w = 25,000$.

Both PA4,6 and PPS were dried in a vacuum oven at 80°C for 2 days. They were blended in a miniature mixing machine (CS-183 MM, Custom Scientific Instruments) at 310°C for 5 min. To obtain the phase diagram in the quiescent state, the blended sample was pressed between two cover glasses at 310°C and then annealed at the desired temperatures for 30 min or less in order to prevent thermal degradation. Nitrogen gas was purged during the experiment. The cloudiness of the polymer blend was observed by eye and the optical microscope. For the shear experiment, the blended samples, with a diameter of 4 cm and thickness of 0.5 mm, were prepared in a hot press (Techno-supply) at 310°C .

A schematic illustration of our shear apparatus is shown in Fig. 1 (16). The sample is located between two parallel glass plates with the upper plate fixed and the lower plate rotated at different rotation speeds. The lower rotating glass plate is restricted inside a copper ring attached to the driving gear, and the upper glass plate is fixed inside a copper cylinder. The copper cylinder and the copper ring can be moved and taken out from the hot chamber. Nitrogen gas was purged into the hot chamber during the experiment. The simple shear flow is generated in the sample by applying constant rotation speeds. During the experiment, the shear-induced phase mixing or demixing takes place at different radii according to the values of applied shear rate. The shear apparatus was designed to observe the sample under shear by two methods; the first by directly observing the sample through the upper window of the shear apparatus and the second by a video recording camera connected to a monitor through a mirror fixed below the lower window of the shear apparatus. Temperature and rotation speed are controlled by the programmable control box. For parallel plate measurement, the shear rate, $\dot{\gamma}$ (sec^{-1}), is a linear function of the radius given by:

$$\dot{\gamma} = \omega \times r/h$$

In the above equation, ω (rad/sec) is the angular velocity, r (mm) is the distance from origin, and h (mm) is the thickness of the sample. $\dot{\gamma}$ (sec^{-1}) has a maximum value at the outer edge of the disk ($r = 20$ mm) and decreases to zero at the center of the disk ($r = 0$).

Once the measurement is finished, the two plates can be released very rapidly to allow a rapid quenching for freezing the morphology under shear flow. The morphology of the sample was observed by an optical microscope and a light scattering apparatus.

Three samples with different compositions, i.e., PA4,6/PPS 80/20, 50/50, and 20/80 wt.%, were used to study the effect of the shear flow as a function of temperature and shear rate.

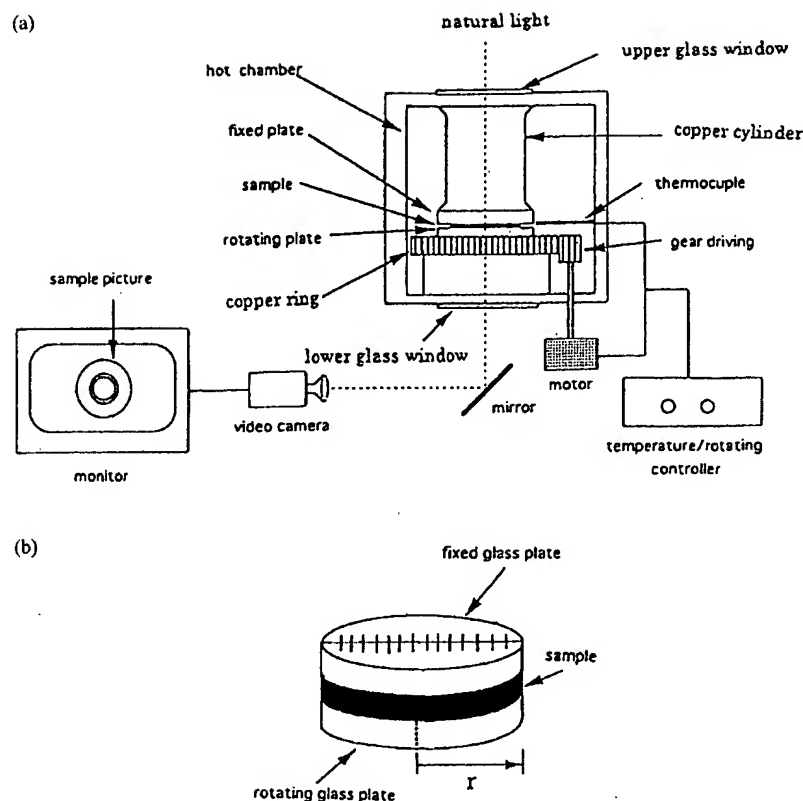


Figure 1. (a) Schematic representation of the shear flow apparatus used in this work. (b) Sample inside the two parallel glass plate.

RESULTS AND DISCUSSION

The phase diagram of PA4,6/PPS blend in the quiescent state was confirmed. The phase diagram was measured by optical microscopy from above the melting temperature of the blends to 400°C, which is close to the degradation temperature, for the three compositions of PA4,6/PPS 80/20, 50/50, and 80/20. For all the measured region, the polymer blends were opaque. If the blend of PA4,6/PPS were miscible at these temperature, it would be difficult to obtain a single-phase mixture because our experiment started from a two-phase mixture, and thermal degradation may take place faster than the dissolution to a single-phase. At any rate, the single-phase region could not be observed before thermal degradation.

The values of solubility parameter calculated by Small's method (23) are 12.4 and 11.9 (cal/cm³)^{1/2} for PA4,6 and PPS, respectively. The difference is 0.5 (cal/cm³)^{1/2}, which is not so large. However, the difference is enough for immiscibility in high molecular weight mixtures.

Figure 2 shows a schematic representation of the sample observation in the polymer blend of PA4,6/PPS 80/20 under simple shear flow at a rotation speed 6.3 rad/sec, as obtained by direct observation. As shown in Fig. 2(a), the specimen became transparent beyond 1.2 cm ($\dot{\gamma} = 150 \text{ sec}^{-1}$) at 310°C, though the inside was still opaque. This means that the polymer blend of PA4,6/PPS 80/20 becomes a single phase under the effect of shear-induced phase mixing above a shear rate of 150 sec^{-1} (the critical shear rate), while the polymer blend is still in the phase-separated state below a shear rate of 150 sec^{-1} . The critical shear rate increases with increasing temperature. As shown in Fig. 2(b), the specimen became transparent outside 1.5 cm ($\dot{\gamma} = 189 \text{ sec}^{-1}$) at 320°C. Shear-induced phase mixing could not be observed for the other compositions, PA4,6/PPS 50/50 and 20/80, for the same conditions.

According to the above shear experiments, the phase diagram of PA4,6/PPS changes under simple shear flow and depends on the shear rate. Figure 3 shows the phase diagram of PA4,6/PPS blend under different shear rates. In Fig. 3, the crosses (x) and the open circles (o) indicate cloudy (immiscible) and transparent (miscible) points under shear flow, respectively. The specimen with PA4,6/PPS 80/20 composition shows miscibility at 310 and 320°C above shear rates of 150 and 189 sec^{-1} , respectively. On the other hand, in PA4,6/PPS 50/50 and 80/20 a miscible region was not observed for the same conditions. Unfortunately, measurements above 330°C and below 310°C were not possible. After sample insertion, it takes a sufficiently long time for the chamber temperature to reach 330°C or higher that thermal degradation could not be prevented. We could not measure the miscibility change below 310°C, because the blend did not have enough mobility to undergo shear due to the high viscosity of the blends.

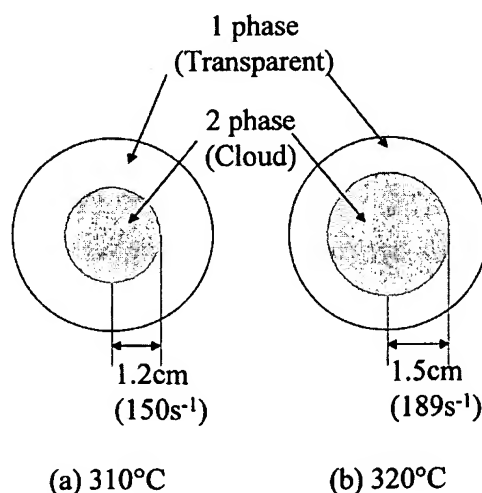


Figure 2. Schematic representation of cloud region in PA4,6/PPS (80/20) blend between parallel plates under the simple shear flow. The shadow region is opaque (a) 310°C and (b) 320°C.

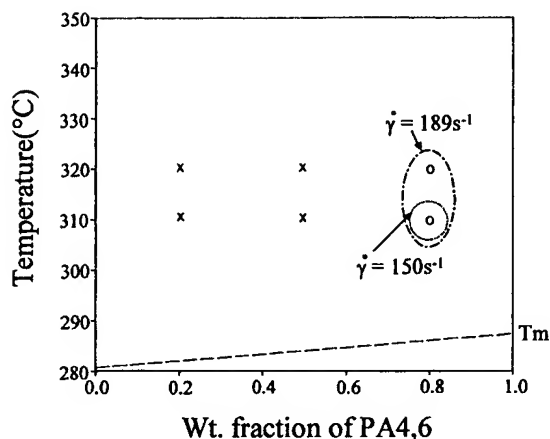


Figure 3. New phase diagram of PA4,6/PPS blend under simple shear flow. The lines of phase boundary at $\dot{\gamma} = 150$ and 189 sec^{-1} are drawn arbitrarily because the shape of the phase diagram is not clear at present.

In Fig. 3, we drew the shape of circle and ellipse as miscible (single-phase) regions for $\dot{\gamma} = 150$ and 189 sec^{-1} , respectively. The miscible region increased with increasing the shear rate. However, these regions were drawn quite arbitrarily since we cannot measure it at other temperatures. This can be considered as a lower critical solution temperature (LCST) type phase diagram, in which the two-phase region is located at higher temperature than the single-phase region and shifts to higher temperature with shear rate.

In order to observe the morphology change with shear rate, after 10 min of the shear experiment the sample was quenched into an ice water bath very quickly. Four locations in the quenched sample were selected at radii 0, 0.5, 1.0, and 1.5 cm; these correspond to shear rates 0, 63, 126, and 189 sec^{-1} , respectively. The phase morphologies of the quenched samples were observed in an optical microscope at room temperature. Figure 4 shows the quenched morphologies of sample PA4,6/PPS 80/20 sheared at 310°C for 10 min. The domain size of the PPS-rich phase gradually decreases with an increase in the shear rate from (a) to (c). The phase contrast between the domain of the PPS-rich phase and the matrix of the PA4,6-rich phase also decreased gradually with increasing shear rate. However, the phase-separated structure still appeared below the critical shear rate ($\dot{\gamma} < 150 \text{ sec}^{-1}$). These immiscible regions were also opaque during direct observation of the shear experiment. Finally, in Fig. 4(d) the phase-separated morphology disappeared above the critical shear rate ($\dot{\gamma} > 150 \text{ sec}^{-1}$), resulting in a single-phase state. This miscible region was transparent during direct observation of the shear experiment. They thus well match the results of the shear experiment in Fig. 2.

On the other hand, we could not find the effect of the shear-induced phase mixing during direct observation of the shear experiment at other compositions.

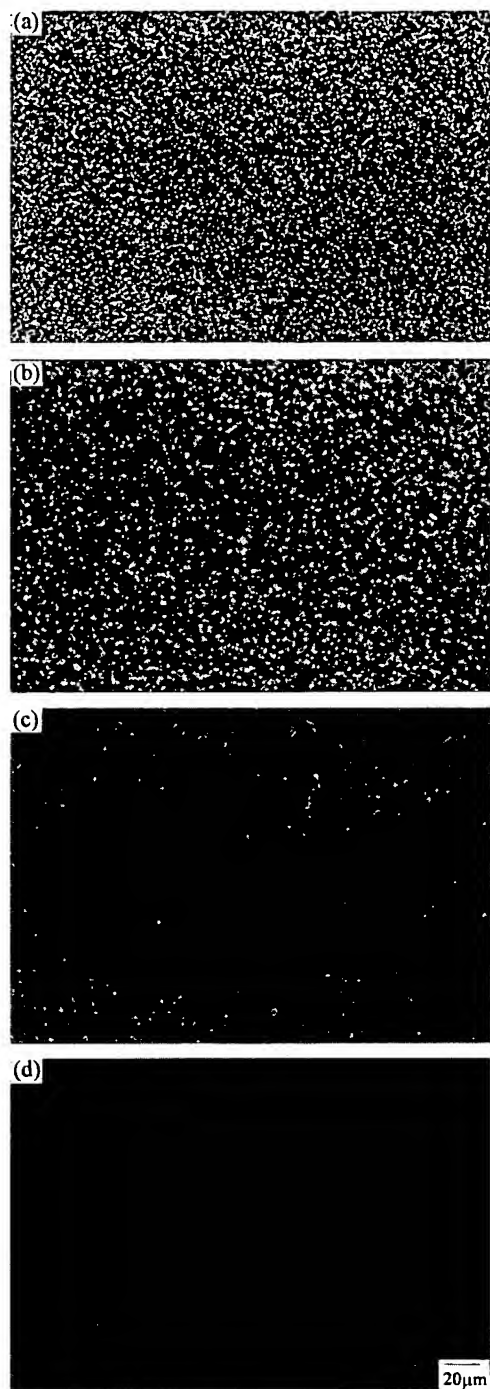


Figure 4. Optical micrographs of PA4,6/PPS (80/20) blend quenched after shearing at 310°C. $\dot{\gamma}$ = (a) 0 sec⁻¹, (b) 63 sec⁻¹, (c) 126 sec⁻¹, (d) 189 sec⁻¹.

Figures 5 and 6 show the quenched morphology of samples PA4,6/PPS 50/50 and 20/80 sheared at 310°C for 10 min, respectively. Both the 50/50 and 20/80 compositions still showed the phase-separated morphology not only at the low shear rate but also at high shear rate, though the domain size at a higher shear rate is smaller than at a lower shear rate. Shear-induced phase mixing did not take place in these compositions even at a shear rate of $\dot{\gamma} = 230 \text{ sec}^{-1}$, which was the maximum shear rate under our experimental conditions. It is very difficult to induce shear-induced phase mixing just from the change of domain size in a polymer blend. However, at higher shear fields, such as in an extruder etc., it is expected that the miscible region would be enlarged.

To observe phase separation from the single-phase without shear flow, namely the recovery of immiscibility in the quiescent state, a sheared sample was annealed in a hot chamber just after shear cessation. A sample of PA4,6/PPS 80/20 was sheared at 310°C for 5 min with the miscible region appearing above the critical shear rate ($\dot{\gamma} > 150 \text{ sec}^{-1}$) and then held at 310°C for 10 min in the hot chamber without shear flow. The change in clarity of the sample was observed by direct observation; the area of the transparent region decreased gradually with time until the entire sample became opaque. It means that the single-phase region induced by the shear flow phase separated again during annealing. After this

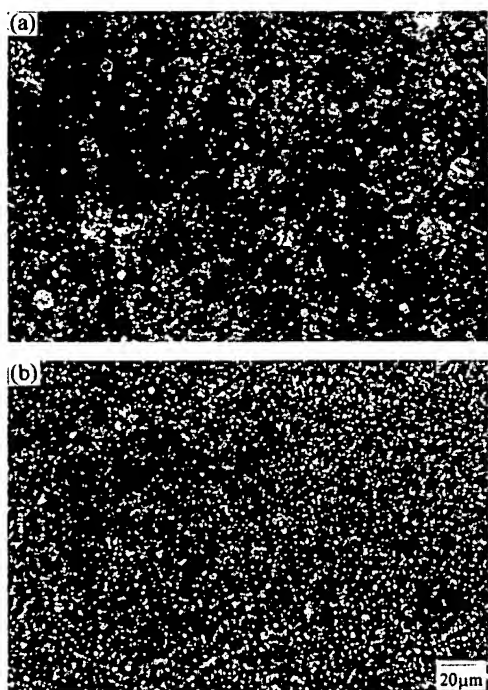


Figure 5. Optical micrographs of PA4,6/PPS 50/50 blends quenched after shearing at 310°C. $\dot{\gamma} =$ (a) 63 sec^{-1} , (b) 189 sec^{-1} .

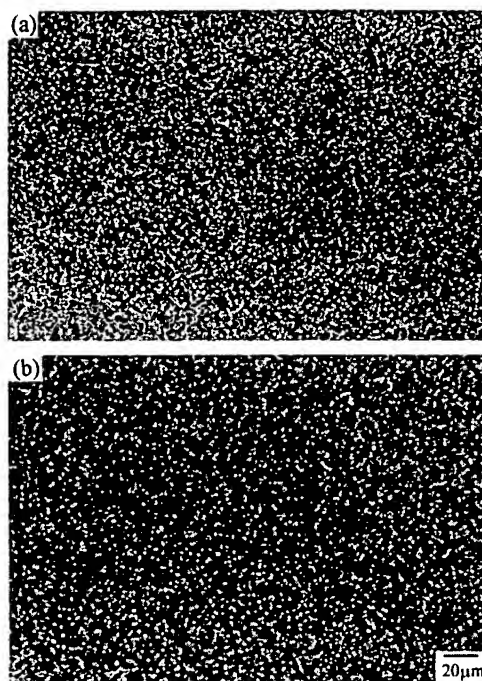


Figure 6. Optical micrographs of PA4,6/PPS 20/80 blends quenched after shearing at 310°C. $\dot{\gamma} =$ (a) 63 sec^{-1} , (b) 189 sec^{-1} .

annealing for 10 min in the hot chamber, the sample was quenched into the iced water bath very quickly. Figure 7 shows the quenched morphology of the annealed sample after the cessation of shear. It shows a regular phase-separated morphology. This structure is the characteristic of phase separation via the spinodal decomposition mechanism and usually forms when the phase separation

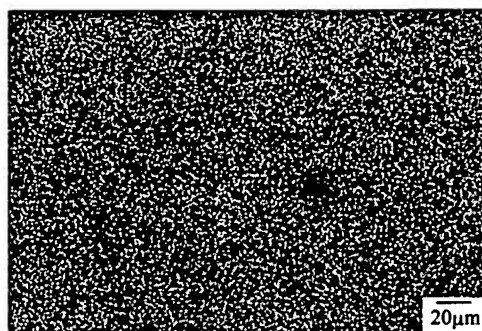


Figure 7. Optical micrograph of PA4,6/PPS 80/20 blend quenched after annealing in hot chamber for 10 min at 310°C without shear flow. The sample was single-phase state under shear flow.

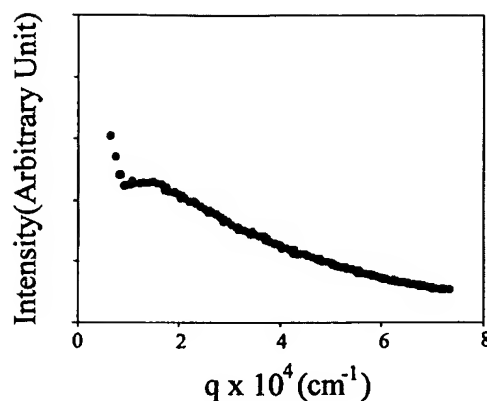


Figure 8. Light scattering profile of PA4,6/PPS 80/20 blend annealed for 10 min at 310°C in quiescent state after the sample of single-phase state under shear flow was quenched into ice water bath.

starts from a single-phase state. Thus, this structure means the recovery from the single-phase state under the shear flow to the two-phase state.

To confirm this phase-separation behavior in the quiescent state, a light scattering measurement was carried out for PA4,6/PPS 80/20. The miscible sample quenched after the cessation of the shear was pressed between two cover glasses on the hot stage of a light scattering apparatus set at 310°C and then annealed for 10 min. Figure 8 shows the light scattering profile. The peak is the result of a ring pattern in light scattering, which is due to some regularity (modulated structure) in morphology suggesting that the phase separation took place via spinodal decomposition. The morphology of this sample observed by an optical microscope was almost the same as that of Fig. 7. The characteristics of this morphology are the periodicity and dual connectivity of phases. Such a well-developed modulated structure could not be attained by a simple mechanical mixing of immiscible systems but formed when the phase separation starts from single-phase state. Thus, it may be attained only by spinodal decomposition from a single-phase mixture prepared under a high shear rate in the mixer.

From the above, it is assumed that this regular phase-separated morphology which is co-continuous or well-dispersed, fine, sea-island induces good physical properties in blends. It is expected that the miscible region would be enlarged in higher shear fields under processing. Probably this is the reason this blend is used industrially without any compatibilizer.

CONCLUSIONS

Though PA4,6/PPS blend is immiscible in the quiescent state, it was found that a small miscible region appeared at high shear rate. The shear-induced phase

mixing took place in a PA4,6/PPS 80/20 composition above the critical shear rate ($\dot{\gamma} > 150 \text{ sec}^{-1}$ at 310°C and $\dot{\gamma} > 189 \text{ sec}^{-1}$ at 320°C). The critical shear rate increased with increasing temperature, with the miscible region increasing with shear rate. The recovery of immiscibility (phase-separation) in the quiescent state was confirmed for a single-phase state specimen formed under shear flow. By annealing after the cessation of the shear, phase separation took place via spinodal decomposition and a well-developed, modulated structure was formed. It is proposed that the regular, phase-separated morphology, produced by the improvement of the miscibility in the shear field, induces good material properties.

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